STATIC ELECTRICITY PHENOMENA

IN THE MANUFACTURE AND HANDLING OF SOLID PROPELLANTS

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The studies described herein show that capacitive discharges and constant potentials may ignite the combustion of composite propellants.

The results analysis allowed SNPE to point out criteria based upon percolation phenomena and specific laws of volumic resistivity as a function of temperature. The above criteria should be able to predict, - with a rather good approximation, - the behavior of some propellants in regard to static electricity.

1. INTRODUCTION.

Within the safety conditions improvement framework, SNPE has tried to evaluate the margins of safety in presence of static electricity. Various measurements, performed in the workshops, have highlighted the presence of static electricity during some operations.

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Significant electric charges were observed on inhibitors and packings material, it has been possible to record the electric potential accumulated on a core during the core pull out operation. The above potential may go up to several thousands of volts at the end of the pull out operation. Thus, SNPE has emplemented a large set of preventive operations which seem to be efficient such as, for instance, the use of graphit and systematic grounding of inhibitors. In the field of safety, preventive operations cannot provide an absolute warranty for any hazard.

Therefore, in the event of electric charges generation, SNPE has tried to understand the behavior of propellants, and more particularly of composite propellants, whith regard to electric discharges.

2. CAPACITIVE DISCHARGE TESTS.

2.1. Presentation :

At the beginning of the study worked out by SNPE we had at our disposal an electric spark priming test wich had been used for a long time by most of the pyrotechnical plants which have to characterize primer explosives in regard to static electricity. The principle of the testing,(sketch depicted in figure 1) consist to determine the minimum energy for which twenty no reaction successive tests were performed. It is understood that the application of an immediate upper energy, would generate a reaction.

This test, involving a maximum energy of 726 mJ (i.e. a 3000 - pF capacity charged under a 22-KV voltage) does not result in the ignition of solid propellants whatever may be their configurations : either on a chipped form or on a pellet form similar to the dimensions of the negative electrode recess.

It should be noted, however, that propellant pellets are sometimes perforated in their center, after a capacitive discharge.

The analysis of the first results lets us assume that the ignition of some propellants would be possible, should the values of the following parameters be increased :

- size of samples (masse effet)
- duration of discharge in the RC circuit (R is used as the propellant resistance, and C as the capacity applied to the propellant extremities (time required for ignition),
- energy delivered.

In view of the above parameters, an equipment was created, it is depicted in figure 2.

The propellant sample to be tested is a cylindrical 90 mm diameter grain and 100 or 200 mm long (investigation of the constant of time impact RC = f (L). C). The grain was located between two electrodes. The electrode system is a "point-plane type" (1) to a sharp area is more intense. In order to get an adequate contact and distribution of the electric current, the rounded surface of the propellant grain facing the negative circular electrode is coated with a silver lacquer.

In order to investigate the influence of ambient hygrometry, the propellant grain was placed inside a $4.10^{13}\Omega m$ volumic resistivity plexiglass chamber.

In order to measure the current accross the propellant grain an adequate resistor following the negative electrode was inserted into the discharge circuit. The electric equipment could deliver a 15.6 Joules energy (i.e. a 34. 7-nF capacity charged under a 30-KV voltage).

2.2. Results.

A lot of tests were conducted and the main results are described here under :

2.2.1. - some propellants react and the reaction can take two forms :

. Ignition : films taken at 2000 frames per second show that, during ignition, cracks appear in the propellant. Through the above cracks, thick bursts of flames are generated. Then the combustion spread out.

(1) which is very penalizing because the electric field close.

According to the sharp noises heard, reactions are very severe most of the time.

. Cracking : the no - ignition tests after discharge show large cracks. These cracks, according to X-ray pictures, were made of a large quantity of small ducts (approximately 5/10 th mm diameter).

Outside, the cracks appear mostly on the lateral surface and on the silver-coated rounded surface. The sketch of figure 3 shows a cracked propellant grain.

On the other hand, it should be pointed out that the cracking phenomenon took place always before the ignition phenomenon.

2.2.2. - the reaction is very casual and may happen after successive capacitive discharges. (number of discharges is called n). For example, a propellant grain may crack at the 2nd and at the 10th discharge and may ignite only at the 20th one.

However, it was observed that usually n is less than 30.

2.2.3. - in case of no reaction the discharge current complies with the Ohm's law i.e. the measured time constant almost equals the time constant calculated in accordance with the relation : $\tau = RC$, C is the capacity applied to extremities of the propellant grain and R the propellant grain resistance.

Calculation of resistance R is based on the geometric dimensions of the grain and on the volumic resistivity measured by a KEITLEY-type cell (this measurement is taken on a 90 mm diameter and 5 mm thick propellant slice).

2.2.4. - In case of reaction, the measurements of discharge currents show that cracking or ignition phenomena appear as soon as the outside capacity is connected to the propellant grain extremities .

During the ignition phenomenon, the current shifts from 0 to several amperes within a few microseconds.

After cracking the current generally becomes 1000 times higher than measurements conducted prior to cracking. Therefore, cracks degrade the propellant and lower down the volumic resistivity. Typical examples of discharge currents are shown in figure 4.

2.2.5. - Parameters such as :

. block length (100 to 200 mm),

. presence of inhibitor,

. outside hygrometry,

do not seem to have an important impact in the above tests.

2.2.6. - The casual nature of the results cannot allow to estimate a minimum energy of non-reaction, for a given propellant.

For this type of test, it should be noted that some propellants ignite at an 100 mJ energy level, approximately. This energy was calculated in accordance to the equation $Q = \frac{1}{2} CU^2$.

2.2.7. - Composite propellants (tested so far), with a volumic resistivity from 10^5 to 10^6 Ωm, do not react to a maximum energy of 15.6 joules.

2.2.8. - Composite propellants, with a volumic resistivity ranging from 10^8 to 10^{11} Ωm, are likely to react to capacitive discharges. In that case, the resistivity is not a discrminative criterion in regard to sensitivity to discharges.

2.3. Analysis.

In compliance with above results, a discriminating procedure was worked out : 3 identical grains from the same composition are submetted to 30 (above 30 it was noticed that the probability of ignition is virtually non-existent) 15.6 Joules (i.e. a 34.7 nF capacity under 30 KV).

A composition is called sensitive to capacitive discharges when, out of the 90 discharges, at least one cracking phenomenon is observed.

3. CONSTANT POTENTIAL TESTS.

3.1. Presentation.

Based on the observation that the reaction starts as soon as the capacity is connected to the propellant grain extremities, it is assumed that application of one voltage step (without capacity) would be sufficient to generate similar effects. For that reason, a second coupling shown in figure 5 was developped.

The cylindrical, 90 mm diameter and 100 or 200 mm long, propellant grain, the round surfaces of which were coated with a silver lacquer, is plaeed, along the symetric axis, between two plane circular electrodes.

The constant potential was applied by 2-KV increments every five minutes in order to verify the influence of the joule effect.

3.2. Results.

3.2.1. - Propellants reacting to the capacitive discharge test, also react as soon as a potential, is applied. The above potential is callėd critical potential. The reactions are similar to the above ones.

3.2.2. - Conduction current, described in figure 6, complies whith the Ohm's law below the critical potential. Occassionnally, before the applied potential reaches the critical potential level, the current is submitted to "variations".

For most of the tests, the reaction is obtained as soon as the modification of the voltage level is applied.

A test, for which the last voltage level applied was very close to the critical potential, shows a very specific conduction current (see figure 7).

Starting from the 12-KV level and after a one minute période of time, pulses period of which are approximately constant, are noticed. The period value is close to the measured time constant of the propellant considered ($\simeq 1,2$ s) amplitude of which exponentially incréases. Each of these pulses was accompanied by a sharp snapping noise.

After a 2-minute period of time, a large crack is observed and the current stabilized at a 3,5 mA value, i.e. 1000 times the value of the initial current.

Then again, reactions are casual and it is very difficult to evaluate a propellant dielectric strength K such that :

$$K = U_c/L$$

where U_c is the critical potential and L the lengh of the propellant grain.

3.2.3. - Some propellants ignite at very low voltage, aróund 1 KV.

3.2.4. Even during long periods of time (30 minutes) the joule effect which may be characterized by the equation : $E = RI^2t$, does not cause any reaction.

4. <u>ASSUMPTIONS ABOUT THE REACTION MECHANISM</u>.

For propellants classified as "sensitive to capacitive discharges", the analysis of the facts such as, for example, initiation of the cracking phenomenon prior to the ignition phenomenon, let assume that the reaction mechanism is divided into two main phases :

- 1st phase : initiation of the cracking phenomenon in connection with a critical potential U_c.

- 2nd phase : initiation of an ignition phenomenon in connection with a critical energy E_c.

The above is explained in figure 8.

All the facts combine to prove out that the reaction starts inside the propellant material. The reaction start is located in microscopic areas. As a matter of fact, if the propellant, in its general form, may be considered as an isotropic environment, this is no longer true at the level of various particles such as aluminum, ammonium perchlorate, etc.

The existence of a critical potential shows that cracking is caused by one or several electric phenomena.

Among the well-known electric phenomena such as semiconduction (case of the ZENER diode which becomes conductive at a given potential by avalanche effect), piezo-électricity, micro-breakdown (between two conductive particles separated by a dielectric) it is assumed that micro-breakdown can be considered as the most probable because the two following observations are support any this hypothesis.

- The measurements of volumic resistivity of aluminum powder (used for propulsion) packaged in a plexiglass tube show that, for a critical potential, the value of resistivity shifts from 10^7 to 10^3 Ωm. This corresponds to a breakdown, for a number of particles, of the alumina layer that covers pure aluminum particles on approximately 40 Å thickness.

- Assuming that the electric diagram for a propellant grain is a dielectric with a parallel RC circuit, it can be imagine that this grain is a complex assembly of RC circuits and that the junction points are conductive particles (e.g. aluminum grains).

Admitting that the breakdown between two conductive points, results in the destruction of the dielectric connection between these two points, and setting up arbitrary initial conditions, it can be proved, by simulation with electronic components or by calculation, that a U potential applied to the extremities (see sketch shown in figure 9) can produce a current (layout is depicted in figure 10). It must be noted that the above layout looks like figure 7 layout.

5. DETERMINATION OF A CRITERION BASED ON RESISTIVITY AS A FUNCTION OF TEMPERATURE.

Over all the compositions tested, the volumic resistivity measurements, from -40 to + 80°C (-40 to + 176°F) show that 3 different laws of resistivity may be encountered versus temperature. The laws, shown in figure 11 are represented by one or two straight lines (1 and 2) with different slopes and equations as follows :

$$\mathrm{Ln}\ (\rho v) = \frac{E}{KT} + \text{constant}$$

where : T = absolute temperature in K degree
K = BOLTZMANN's constant
E = energy in eV.

This law is similar to semiconductors. The existence of 2 straight lines points out a change in the type of conduction starting from a given transitional temperature. The values of the energies calculated from the slopes of the straight lines range from O to 2 eV.

The most remarkable observation is that the compositions which react to capacitive discharges follows a type-I law (i.e; the proportion E_1/E_2 is above 1) where as the compositions which do not react have a type II or III-law (i.e. the proportion E_1/E_2 is lower or equal to 1).

6. DETERMINATION OF A CRITERION BASED UPON PERCOLATION.

A factorial investigation of the propellants active constituents was carried out. A compromise between a strict investigation of parameters and the feasibility of specific formulations was worked out.

The results of this investigation mainly enphasize :
- the aluminum particle size.
- the electric characteristics of the binders (binder = prepolymer + miscellaneous additives).

Since the aluminum granulometry is concerned, and for a constant aluminum content the decrease in diameter of aluminum particle size, (i.e. their increase in number), results in sensitive to capacitive discharges compositions.

The impact of the number of conductive particles was quite naturally the next step to investigate percolation phenomena.

Percolation, as theoretically defined, is independent of the voltage applied and allows - (for a given conducting and insulating particle system) - to determine the critical level of Nc/Ni ratio (Nc = number of conducting particles and Ni = number of insulating particles) above which the entire system is fulling conducting.

In the case of a composite propellant, it does not seem possible to obtain such a level, because aluminum particles are working as insulations, although conductive inside.

In fact, the phenomenon that we have to work with comes from theoretical percolation phenomenon and, therefore, a "P breakdown percolation" coefficient was defined as follows :

$$P = \frac{Nc/Ni}{\sigma_L V_L}$$

where : σ_L = binder conductivity
V_L = binder unit volume

The above coefficient covers 9 parameters.

Currently, the validation phase was conducted over about fifty different formulations. It is now possible to know a range for the critical P value : above this value, formulàtions are sensitive to capactiive discharges, under they are not.

However the above critical P value is not clean and there remains an area where this criterion is uncertain.

CONCLUSION.

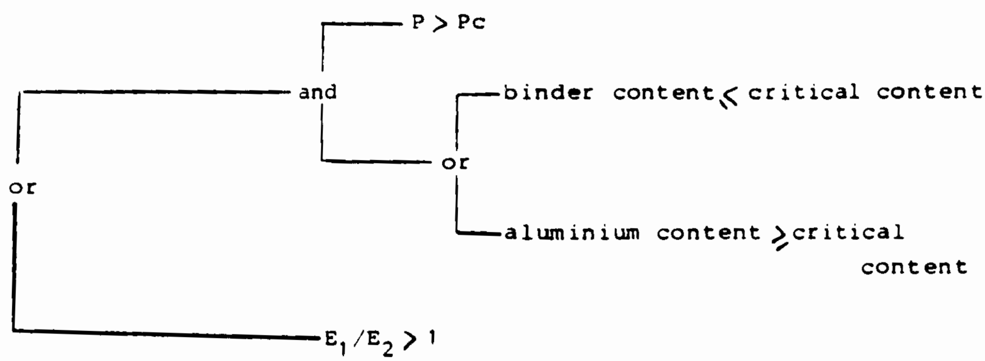
As we tried to demonstrate, it looks probable that the reaction mecanism is, first, conducted by a micro-breakdown phenomenon.

In order to understand this mecanism, a theoretical and fondamental study will be worked out.

Critical electrical fields between particules will be more specially studied.

To currently carry out our safety problems, two empirical criteria may be used, one is based on percolation phenomenon, the other is based on specific resistivity laws versus temperature.

So, a propellant will be classifed as sensitive to static electricity if the following conditions are carried out.



Above criteria are systematically applied during new formulations developpements. Propellant behaviour may bé anticipated and may be modified if necessary so that safety cautions are taken to prevent any risk either dúring conception or carrying out of the materials.

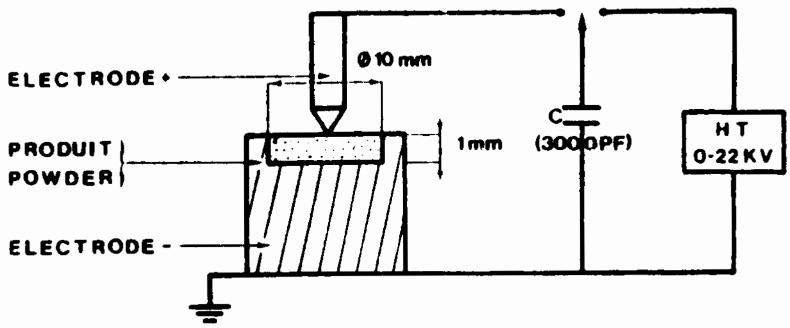


fig 1

Schematic arrangement of ignition test by electrostatic spark

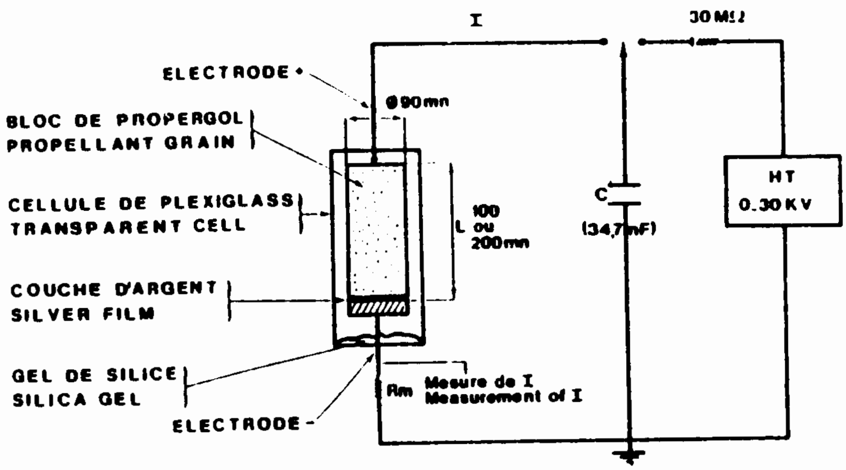


fig 2

Schematic arrangement for capacitive discharges test on the propellant grains

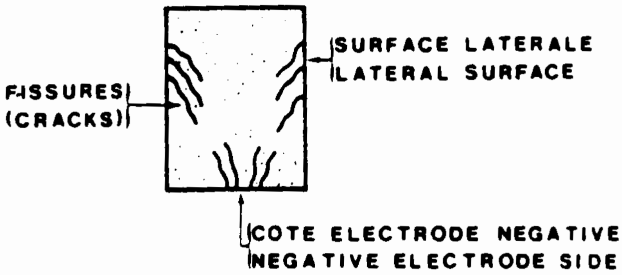


fig 3

Schematic diagram of a cracked propellant grain

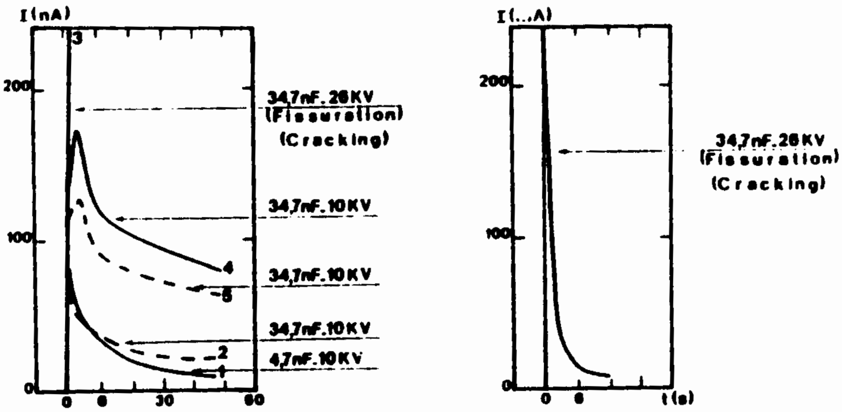


fig 4

Curves of discharges current (I) versus time (t) for different discharges(6) in a "sensitive" propellant

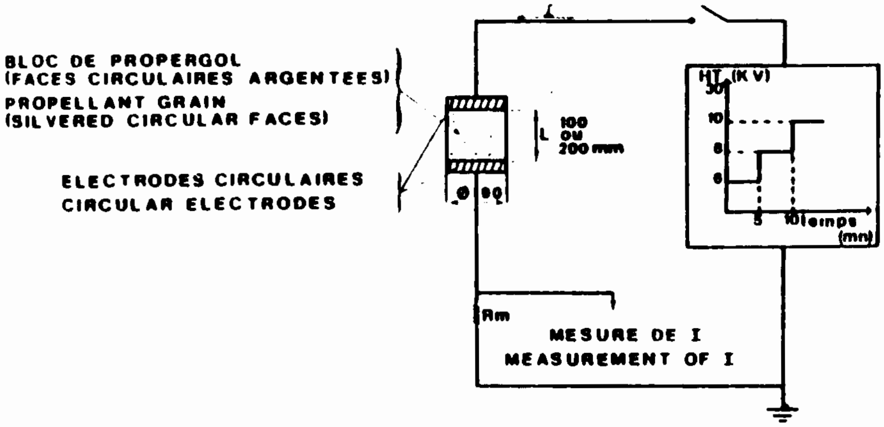


fig5
SCHEMATIC ARRANGEMENT FOR POTENTIAL TEST

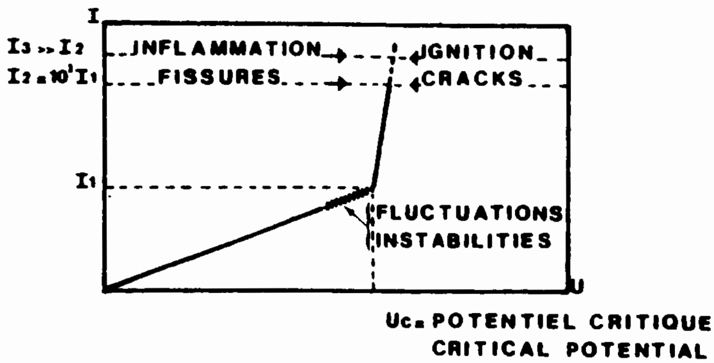


fig6

General evolution of conduction current (I) versus potential (U)

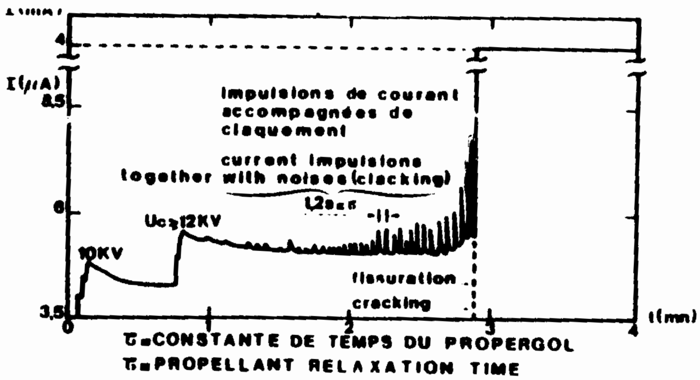


fig7

Typical curve of conduction current (I) versus time(t) in a "sensitive" propellant (initial ρv = 10[9] Ωm)

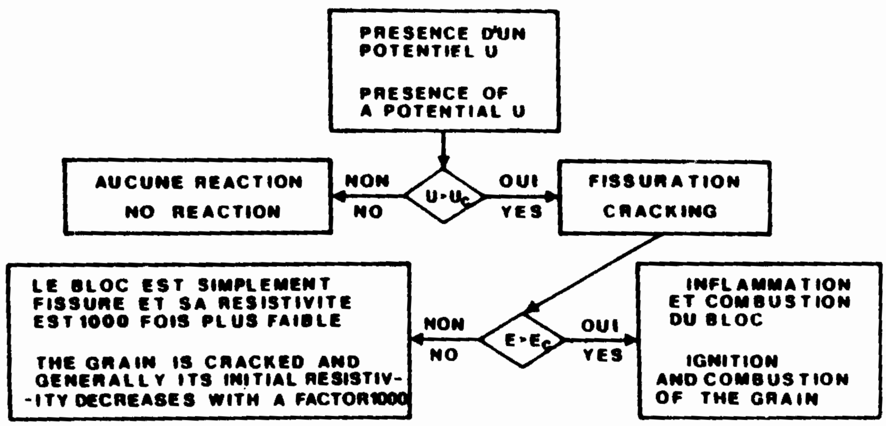


fig8

Schematic diagram of the reaction mechanism

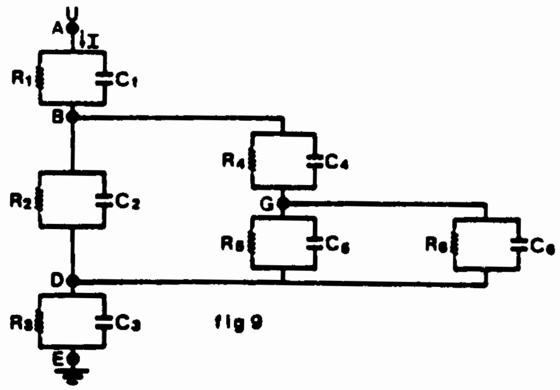


fig 9

Schematic diagram of a complex system of RC circuits

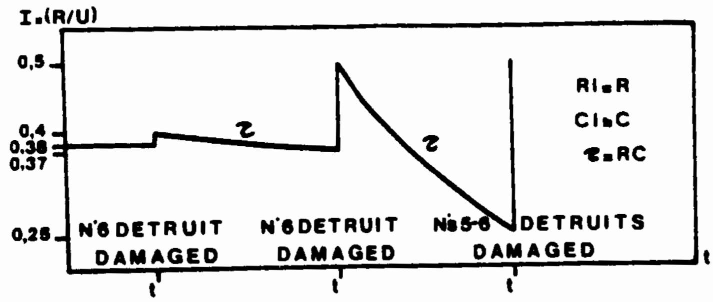
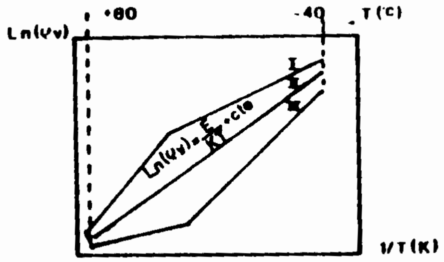


fig 10

Evolution of current (I) versus time(t) circulating from point A to E

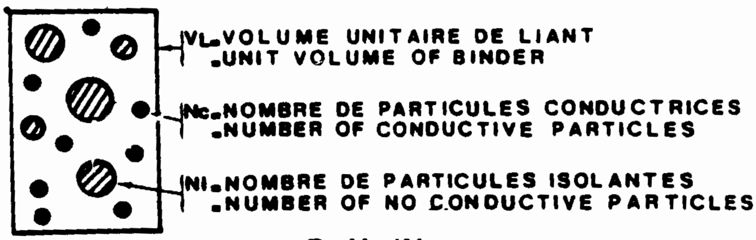


LOI I = PROPERGOL "SENSIBLE"
LAW I = "SENSITIVE" PROPELLANT | $E_1/E_2>1$

LOIS II ET III = PROPERGOL "NON SENSIBLE"
LAWS II AND III = "NO SENSITIVE" PROPELLANT | $E_1/E_2<1$

fig11

Volumic resistivity(ρv) as fonction of $\frac{1}{T}(K)$



$$P = \frac{N_c/N_i}{\sigma_L/V_L}$$

σ_L: CONDUCTIVITE DE LIANT
CONDUCTIVITY OF BINDER

fig 12

Definition of the "breakdown percolation" coefficient (P)